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Methods for Determining the Hydrogen-ion Concentration of Soils

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REVIEW OF LITERATURE

Methods for the electrometric and colorimetric determination of the hydrogen-ion exponents of soils were published by Gillespie (*29*)[1] in 1916, and the occurrence of truly acid soils was demonstrated. Of fundamental importance was this first comparison reported between results by two different methods which showed substantial agreement. In an article of subsequent publication by Sharp and Hoagland (*59*) an electrometric procedure for the determination of the hydrogen-ion exponents of soils was given, along with a detailed discussion of several phases of acidity and adsorption. Prior to this few similar measurements had been made of this intensity factor of acidity in soils. Mention may be made, however, of a few earlier electrometric measurements by Saidel (*56*) on boiled alkaline extracts and by Fischer (*25*), whose measurements were made with the hydrogen electrode. These measurements, in order to obtain constant potentials, were continued for seven or eight hours.

PHYSICO-CHEMICAL ACIDITY

Preliminary to considering the methods, it may be well to discuss briefly the physico-chemical significance of acidity.

[1] Numbers in parentheses refer to "Literature cited," p. 26.

Water dissociates into hydrogen-ions H^+ and hydroxyl-ions OH^-, the former being characteristic of acids and the latter of bases, the reversible reaction being represented as follows:

$$HOH \rightleftarrows H^+ + OH^-$$

According to the law of mass action this reversible reaction at equilibrium is represented by the following equation:

$$\frac{[H^+]\,[OH^-]}{[HOH]} = k$$

As the concentration of the undissociated water remains nearly unchanged, owing to its very small dissociation, [HOH] may be considered a constant and combined with k, writing the above equation as follows:

$$[H^+]\ [OH^-] = K_w$$

The value of K_w, as given by Lewis, Brighton, and Sebastian (*47*) for pure water is $K_w = 1.012 \times 10^{-14}$ at 25° C., which gives a concentration of $[H^+]$ and $[OH^-]$ equal to 1.006×10^{-7}, or approximately 1.00×10^{-7}. In pure water, the concentration of the hydrogen-ions is equal to the concentration of the hydroxyl-ions, and the resulting condition is one of physico-chemical neutrality. This neutral point probably possesses little other physical significance and is seldom the theoretical or even practical point of titrimetric neutrality. Since the product of the concentrations of the two ions is a constant, approximately 1.00×10^{-14} at 25° C., it is apparent that in any solution, whatever the concentration of the hydroxyl-ions, there must always be present sufficient hydrogen-ions to satisfy the above equation. One may, therefore, refer to any solution, acid or alkaline, in terms of its hydrogen-ion concentration. Instead of expressing the hydrogen-ion concentration as a negative power of 10 there has been introduced by Sörensen (*62*) a pH scale of expression. In the working formula of the hydrogen electrode the potential is related to the logarithm of the reciprocal of the hydrogen-ion concentration $\log \frac{1}{[H^+]}$, and it is to this logarithmic term that the symbol pH is given, thus, $pH = \log \frac{1}{[H^+]}$. Various reasons for this preference of expressing the hydrogen-ion concentration will not be discussed here, as they have been previously given by Clark (*22*).

According to the pH scale (*22*), at approximately pH 7 the hydrogen and hydroxyl-ion concentrations are equal and the condition is one of physico-chemical neutrality. Briefly stated, below pH 7, as the pH values decrease, the hydrogen-ion concentration becomes greater than the hydroxyl-ion concentration; and above pH 7, as the pH values increase, the hydrogen-ion concentration becomes less than the hydroxyl-ion concentration. For each unit decrease in pH the hydrogen-ion concentration becomes ten times each preceding concentration. It is well to bear in mind that the hydrogen-ion exponent is a measure of the intensity factor of acidity and not of the quantity of acid or acid substances present. The relationship be-

tween hydrogen-ion concentrations and pH values is shown in Table 1.

TABLE 1.—*Relationship between hydrogen-ion concentrations and pH values*

$[H^+]$	pH	$[H^+]$	pH
10^{-0}	0	10^{-8}	8
10^{-1}	1	10^{-9}	9
10^{-2}	2	10^{-10}	10
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-12}	12
10^{-5}	5	10^{-13}	13
10^{-6}	6	10^{-14}	14
10^{-7}	7		

In several instances in the literature different investigators have averaged a series of pH values and apparently lost sight of the exponential significance of this term. It is very obvious that in a series of pH values the individual values may be such that their average will approximate the pH value as computed from the average of the corresponding hydrogen-ion concentrations. On the other hand, this averaged pH value may be very different from the correct pH value corresponding to the average of the respective hydrogen-ion concentrations. For example, if the pH values of two soil plots are 5 and 5, the average pH value would be 5, as would also the average of two plots of pH 6 and 4, respectively. In the first instance the pH value corresponding to the average of the respective hydrogen-ion concentrations would also be 5, but in the second instance the average of the respective hydrogen-ion concentrations gives a corresponding pH value of 4.3. The arithmetical averaging of pH values has also been referred to by Wherry (*68*).

FACTORS AFFECTING THE HYDROGEN-ION CONCENTRATION OF SOILS

PERIODIC VARIATION OF HYDROGEN-ION CONCENTRATION

In studying the hydrogen-ion concentration of soils, the time of sampling is apparently of significance, as there have been observed periodic variations in the reaction of the soil. Lipman and coworkers (*48*) found fluctuations of about 0.7 pH in the surface soils of their check plots from May to November. Results obtained by Kelley (*42*) show that over a period of a year monthly tests reveal a fluctuation in the pH value of a soil amounting at times to a pH of 1 in the subsoil as well as at the surface. In the work of Burgess (*18*) seasonal variations were also observed in the pH values of soils. From the results of Baver (*6*) it is apparent that the acid soils show a continual increase in hydrogen-ion concentration from May to September, whereas the alkaline soils show no consistent variations during this period. In the case of the acid soils there was a consistent increase in acidity from the spring to the fall, with a return to nearly the original acidity the following spring. From May to September acid soils varied as much as 0.9 pH and alkaline soils about 0.6 pH. The rainfall and season seemed to be two important factors affecting these variations in the soil reaction.

EFFECT OF DRYING OF SOIL SAMPLE ON THE HYDROGEN-ION CONCENTRATION

Results obtained by the writer on the effect of air drying of soils on the pH value show that air drying of acid soils slightly increases the hydrogen-ion concentration. In this connection Burgess (*17*) found that air drying of acid soils had but little effect on their hydrogen-ion concentration, whereas with slightly alkaline soils it decreases the pH value. This effect was particularly noticeable at a temperature of 103°C. Rost and Fieger (*55*) determined the pH variation resulting from air drying acid and alkaline soils and found that some samples became more acid and some more alkaline, with a general tendency, however, for the air-dried samples to become more acid than the fresh ones. The differences between fresh and air-dried soils, from fields on which liming experiments were in progress, varied from pH 0.03 to 1.17. There was also a general tendency for fresh, moist soils to become more acid when stored for three months in air-tight glass containers. It was concluded that the only reliable indication of field conditions was obtained with soil samples freshly taken. Results obtained by Healy and Karraker (*36*) show that air drying acid soils slightly lowered the pH values. Joseph and Martin (*41*) found that oven drying alkaline soils lowered the pH of the extract, as compared with the extract of the undried soil. This effect, they say, "is probably due to the accelerated effect of the electrolytes caused by increase of temperature and concentration." Results obtained by Biilmann and Jensen (*10*) on 18 soils from about pH 5.2 to 8.3 show the air-dried soils to be slightly more acid than the same soils before air drying. They state: "Our measurements only permit us to conclude that the air-dried soil samples show pH values which correspond essentially to the values found with nonair-dried samples." Kelley (*42*) found that under field conditions drying is apparently often, but not invariably, accompanied by increased acidity. The work of Baver (*6*) shows that the reaction of acid surface soils is not significantly affected by air drying, but that there is a considerable decrease in alkalinity with the alkaline soils. The air drying of subsoils produced a marked increase in acidity, which increased with depth. From the data presented it is evident that fresh samples for hydrogen-ion exponent determinations give a closer expression of soil reaction in the field than do air-dried samples. As stated by Baver, for practical purposes, therefore, it seems that the hydrogen-ion concentration of an air-dried soil is sufficiently accurate, but for refined reaction studies fresh samples should be used.

The general conclusion seems apparent that drying of soils is, as a rule, accompanied by a change in reaction, generally in the direction of increased acidity. The change has a tendency to be more pronounced in alkaline soils.

EFFECT OF GRINDING OF SOIL SAMPLE ON THE HYDROGEN-ION CONCENTRATION

By grinding a soil to pass through a 100-mesh sieve Baver (*6*) found that the hydrogen-ion concentration (quinhydrone electrode) of the acid samples of Wooster silt loam was not materially affected, but that with the alkaline samples the hydrogen-ion concentration was increased. This, it is stated, was probably due to the exposing of

surfaces that had not been affected by the addition of lime. A decrease in acidity was found by grinding Brookston clay and Miami clay, glacial limestone soils. Dunkirk sand showed a large decrease in acidity after being ground. Sharp and Hoagland (*59*) observed, with the exception of one soil, that grinding a soil to pass a 200-mesh sieve did not materially alter the hydrogen-ion concentration of soil suspensions. Out of 5 acid soils, 2 showed no change and 3 showed a tendency toward a decrease in pH value, in one instance a decrease of 0.3 pH. With one alkaline soil, the exception previously mentioned, grinding increased the pH from 6.4 to 7.15. These changes in reaction as a result of grinding no doubt are attributable to the solution and hydrolysis of the minerals in the soil. For the determination of the hydrogen-ion exponents of soils it is preferable, therefore, to use the unground sample.

SOIL-WATER RATIO

In the determination of the hydrogen-ion concentration of a soil the soil solution, suspension, and extract have been employed, the soil suspension and extract, however, being more generally used. The question naturally presents itself, What ratio of soil to water should be used?

A review of the literature reveals a lack of uniformity of opinion in regard to the effect of the variation of this ratio on soil reaction. Sharp and Hoagland (*59*), employing the hydrogen electrode, found comparatively insignificant changes in the hydrogen-ion concentrations when widely varying proportions of water to soil were used. They attributed most of the small fluctuations to limitations of the apparatus. Their electrometric determinations were made on soil suspensions, the duplicate determinations usually agreeing within only 10 to 20 millivolts. Gillespie and Hurst (*32*) found an average positive difference for nine soils of 0.14 pH by varying the water-soil ratio from 1 to 1 to 2 to 1. This would indicate that at optimum moisture content the acidity may be more intense. In a subsequent publication (*33*) the same investigators found that the differences in exponents caused by varying the water-soil ratio are distributed like errors about a mean value of +0.04. There was no apparent correlation between the actual values of the exponent and the difference caused by dilution.

More recently Salter and Morgan (*57*) found that for the soils included in their investigation the pH value at a soil-water ratio of 1 to 5 varied from 0.10 to 0.85 pH higher than the calculated reaction at a field moisture content of 20 per cent. They suggest a soil-water ratio of 1 to 5 as being suitable for colorimetric and electrometric procedures, their electrometric determinations being made with soil suspensions. For the acid soils investigated by these authors their electrometric results indicated a "systematic variation of hydrogen-ion concentration with variations in soil-water ratio, the highest hydrogen-ion concentration occurring at high soil-water ratios, with a progressive decrease as dilution is increased."

More recently Crowther (*24*) has found a regular increase of about 0.1 pH for a twofold dilution, varying the soil-water ratio from 1 to 1 to 1 to 32. Pierre's (*52*) work shows that when the soil-water ratio is varied from 1 to 2 to 1 to 50 the hydrogen-ion concen-

trations of some soils vary, whereas those of others show no differences. From the data it appears that the most acid soils studied are affected more by changing the soil-water ratio, and regardless of the soil texture this relation seems to hold. It is concluded by Pierre (*52*) that soils showing a change in hydrogen-ion concentration at different soil-water ratios do not show these differences after washing out the soluble salts and the more soluble acids. The acidity after washing is due entirely to the relatively insoluble acids. Further data given by Pierre show that the soil solution is not at a higher hydrogen-ion concentration than the 1 to 2 soil-to-water suspension or extract. From these data it is seen that the determination of the hydrogen-ion concentration of such soil suspensions or extracts is the same as that of the soil solution. The hydrogen-ion concentration of the displaced soil solution has been compared with that of the soil suspension by several investigators, and has been found in general to have a higher hydrogen-ion concentration than the soil suspension. This lack of agreement has been attributed by Pierre to the failure of these investigators to obtain the actual soil solution. Barnette, Hissink, and Van der Spek (*4*) concluded that the equilibrium with regard to the hydrogen-ion concentration between soil and water varies with the soil-water ratio and is dependent on many factors. The closer soil-water ratios (thicker suspensions) show a more constant hydrogen-ion concentration, and should, therefore, be used for the hydrogen electrode determination.

Since the soil-water ratio may be considered as more or less arbitrary, the writer has used for air-dried mineral soils the soil-water ratio of 1 to 2 as being well adapted to the electrometric and colorimetric determinations of the hydrogen-ion exponents of soils. For peats or mucks the soil-water ratio may vary from about 1 to 3 to 1 to 7.

EFFECT OF CARBON DIOXIDE ON SOIL REACTION

The effect of the carbon dioxide partial pressure on the hydrogen-ion equilibria will in general depend on the pH value. This effect is small at acidities in the vicinity of pH 5 but increases with the pH (*22*). Hoagland and Sharp (*38*), using the hydrogen electrode, arrived at the conclusion that the hydrogen-ion concentration of acid soil suspensions was little affected when in contact with a carbon dioxide content as high as 10 per cent. However, the hydrogen-ion concentration of slightly alkaline soils showed a small increase, owing to raising the carbon dioxide partial pressure, while soils containing alkali carbonates showed a larger increase. For a clear exposition of the carbonate equilibrium the reader is referred to Johnston (*40*). By passing carbon dioxide in from the bottom of the electrode vessel and allowing it to saturate the soil suspension, and introducing hydrogen from the top only, Pierre (*52*) observed increases in the hydrogen-ion concentration of acid and alkaline soils. The content of carbon dioxide used here is obviously much higher than in the field. By approaching more closely field conditions it was observed that the slow passage of carbon dioxide through the soil in glass percolators, of 800 to 900 grams capacity, for about one-half hour, did not affect the hydrogen-ion concentration of the (water) displaced soil solution. The displaced solution from a

limed quartz sand showed a much higher hydrogen-ion concentration after treatment with carbon dioxide, which was explained by the fact that the sand is poorly buffered.

Biilmann and Jensen (*10*) determined the effect of carbon dioxide on the pH values of nine soils from about pH 4.7 to 8.2, using boiled distilled water free from carbon dioxide, aerated distilled water in equilibrium with the normal carbon dioxide pressure of the atmosphere, and ordinary distilled water without the carbon dioxide being removed. Their data show that the ordinary distilled water containing 17.2 milligrams of carbon dioxide per liter gave, with the neutral and alkaline soils, results about 0.1 to 0.3 of a pH lower than obtained with the boiled distilled water or aerated distilled water, the latter containing 1.0 milligram of carbon dioxide per liter. The differences between the results obtained with the three kinds of water were insignificant with the acid soils. Since the results on all of the soils with the boiled and aerated distilled water were in close agreement, Biilmann and Jensen recommend the use of either boiled or aerated distilled water.

ELECTROMETRIC AND COLORIMETRIC METHODS

The methods for the determination of the pH value may be grouped under the two headings, electrometric and colorimetric. Under the electrometric method may be included the fundamental hydrogen, the quinhydrone, and the antimony-electrode procedures, and under the colorimetric method various adaptations of indicators to the approximate determination of the hydrogen-ion exponent.

OUTLINE OF ELECTROMETRIC METHOD

The application of the electrometric method to the determination of the pH values of soils consists essentially in the measurement, with some type of potentiometer or voltmeter in conjunction with a galvanometer, of the potential difference between a standard electrode, such as a calomel electrode, and the soil as a hydrogen, quinhydrone, or antimony electrode, contact between the two electrodes being made with saturated potassium chloride solution. From this measured potential difference the pH is calculated by aid of a working equation, or with some potentiometers it is so arranged that the pH may be read directly.

DETAILS OF THE HYDROGEN-ELECTRODE METHOD

HYDROGEN ELECTRODES

A piece of platinum wire, foil, or gauze will serve as a hydrogen electrode. The platinum wire and foil are preferable, as the gauze presents cleansing difficulties. If foil is used, and it generally is, it may be welded to a short piece of platinum wire, the wire sealed into a glass tube, and mercury poured in to make contact. The welding may be accomplished by placing the foil and wire in contact on a hard surface and sharply striking with the polished end of a small hammer or tool while heating to redness with a blast lamp. Since the design and size of the electrode permit of many types, mention will be made of only a few. Clark (*22*) recommends a piece of foil

about 1 square centimeter in size for use with his electrode vessel. Sharp and Hoagland (*59*) used a Cottrell hydrogen electrode consisting of a glass tube about 15 centimeters long and 1 centimeter in diameter, in one end of which is sealed a cylinder of fine platinum gauze about 1 centimeter long and near the other end of which a side tube permits the entrance of hydrogen. A platinum wire is affixed to the inside of the gauze and sealed into a central tube through which electrical connection is made. Gillespie's electrode (*29*), shown in Figure 1, consists of a half cylinder of platinum foil 2.5 by 3.3 centimeters, although 1 inch square was satisfactory. The platinum is supported at both ends by leads for the current, thus giving an even deposit of metallic "black." This electrode is simple of construction and is rugged. Knight's electrode (*43*) is a rectangular piece of platinum 1.2 by 2.4 centimeters, with platinum wires welded to each end for sealing to a glass tube. Hildebrand's electrode (*37*, *22*) is somewhat similar to the one used later by Sharp and Hoagland (*59*). Salter and Morgan (*57*) used a platinum-coated glass electrode of the Luther type in a hydrogen cell of about 10 cubic centimeters' capacity.

FIG. 1.—The electrode

It hardly seems necessary to mention that cleanliness of the electrode is very essential. The electrodes are frequently cleansed in hot chromic-acid solution and when not in use are kept in a chromic-acid bath. Cleanliness of electrodes is particularly stressed by Biilmann (*9*) for the quinhydrone electrode, in which case he recommends heating of the electrodes to redness in the alcoholic flame but not in the ordinary gas flame.

PLATING OF ELECTRODES

For plating electrodes solutions of palladium chloride, iridium sesquichloride, and chloroplatinic acid have been used (*1*, *22*, *60*). Palladium is being used rather extensively, as it is easily removed from the platinum electrode by electrolysis in hydrochloric acid. For coating the electrode an approximately 3 per cent solution of palladium chloride containing about 2 per cent of concentrated hydrochloric acid by volume is used, the concentration of palladium being maintained by the occasional addition of fresh palladium chloride. Lightly coating the electrode requires about five seconds. After this it is washed with distilled water and is then thoroughly charged with hydrogen for about 10 seconds in 10 per cent sulphuric acid. Again it is thoroughly washed with distilled water before using. The previous deposit may be easily removed by aqua regia or electrolysis in 1 to 1 hydrochloric acid by reversing the polarity. A current of about 0.8 amperes at 4 volts was used for coating and subsequent treatment of the electrodes and was taken from the 220-volt lighting circuit by using the proper resistances. A 4-volt storage battery or dry cells may also be used, connection being made to platinum electrodes in three small vessels holding the palladium solution and sulphuric and hydrochloric acids.

ELECTRODE VESSELS

Many types of electrode vessels used for the determination of the hydrogen-ion exponents of soils will be found in the literature.

However, in the construction of a vessel there are certain points warranting attention. By shaking the electrode vessel Hasselbalch (*34*) was able to obtain constant potentials in a short time. The application to soils of this principle of shaking the electrode vessel with alternate immersion and exposure of the electrode allows of a speedier attainment of equilibrium between gaseous hydrogen, the electrode, and the soil suspension. Under these conditions a localized equilibrium is avoided, and one more characteristic of the entire suspension is obtained. Shaking mechanically or by hand, bubbling hydrogen or mechanical stirrers have been very generally employed for keeping the soil in suspension.

Clark (*21*) designed a closed type of vessel which has met with considerable general favor. It was rather intended for solutions but was used by Healy and Karraker (*36*) for soils. Knight's vessel (*43*) of 100 cubic centimeters capacity, in which the soil suspension may be agitated continuously, is a tube 3.3 centimeters in diameter and 16 centimeters long, closed at both ends. Near one end is an opening through which is introduced the electrode and hydrogen, and near the other end is a sealed-in tube with stopcock for making contact with the standard electrode. The vessel used by Sharp and Hoagland (*59*) consisted of a wide-mouthed bottle of 75 to 100 cubic centimeters capacity, closed to the air. A vessel recently devised by Bray (*15*) embodies a combination of ideas used in other vessels. It consists of a Gooch funnel or carbon filter tube with the stem bent up and a perforated porcelain plate sealed into the bottom. The hydrogen is bubbled up through this plate rapidly enough to give the soil suspension the appearance of boiling. The bubbling is continued about 13 minutes (the first determination of the day requiring from 20 to 30 minutes bubbling before the electrodes reach equilibrium) after which a reading is made. Another reading is made two minutes later. This author states that electrodes plated once as described are good for from 40 to 60 determinations. The electrode vessel of pyrex glass, used by the writer, is shown in Figure 2. It is a closed type, being a modification of the one employed by Gillespie (*29*) and has a volume of about 70 cubic centimeters. With this vessel the potassium chloride contact is drawn into the end B and any possible contamination of the soil suspension with potassium chloride is avoided.

CALOMEL ELECTRODES

Many variations in calomel-electrode design, each possessing its own features for its particular requirements, will be found in the literature. In general the calomel electrode consists of a layer of pure mercury covered with a layer of pure calomel containing finely divided mercury over which is a definite concentration of potassium chloride (0.1 N, N/1 or saturated) saturated with calomel. Contact with the potassium chloride may be made through a side arm and contact may be conveniently made with the mercury by a sealed-in platinum wire. Recently Schollenberger (*58*) described a calomel electrode, though not novel in design, which the author has found satisfactory in soil work, using the quinhydrone electrode, and which is considered adaptable to electrometric titrations. Liquid contact with the solution under test is made by means of a ground-glass plug.

Various types of calomel-electrode vessels are also illustrated by Clark (*22*) and the methods of preparation are described in detail.

CONTACT BETWEEN THE HYDROGEN AND CALOMEL ELECTRODES

Contact between the hydrogen electrode and standard electrode has been made in a variety of ways (*22*), such as with membranes, flowing junctions, and a mixture of agar-agar with potassium chloride. Since contact of two solutions of different electrolytes produce a potential difference at the plane of contact, it is necessary to use some solution which will minimize this potential. For this purpose a saturated potassium chloride solution is used. In some instances contact is made by means of a capillary tube containing a saturated solution of potassium chloride in direct contact with the soil suspension, but it is well to avoid contamination of the suspension with potassium chloride if possible. The agar tube has been frequently used (*10*, *20*) for making contact and may be prepared by heating 5 grams of agar-agar with 100 cubic centimeters of 3.5 molar potassium chloride solution to almost boiling. This solution is drawn into the clean, dry, connecting tube and is allowed to stiffen. The tubes, which must be entirely filled with the agar mixture, are trimmed off even at the ends. The tubes should be soaked about one hour in distilled water before using and should be kept in contact with the soil suspension only during the reading.

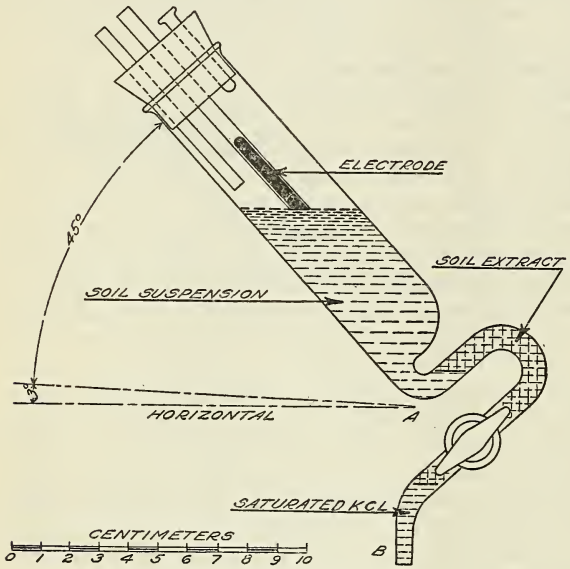

FIG. 2.—The electrode vessel

HYDROGEN-ELECTRODE METHOD

The procedure adopted for the determination of the pH values of soils with the hydrogen electrode is as follows: Fifteen grams of air-dried soil (passing a 2-millimeter sieve) and 30 cubic centimeters of water are shaken vigorously in a large pyrex test tube for approximately one minute. This suspension is allowed to stand a short time for sedimentation, and enough of the supernatant liquid to fill the neck of the vessel and 3-millimeter bore of the stopcock is poured into the electrode vessel. (Fig. 2.) The end B is filled with saturated potassium chloride solution and the vessel is attached to a shaker (fig. 3), the actuating arm of which passes through the axis

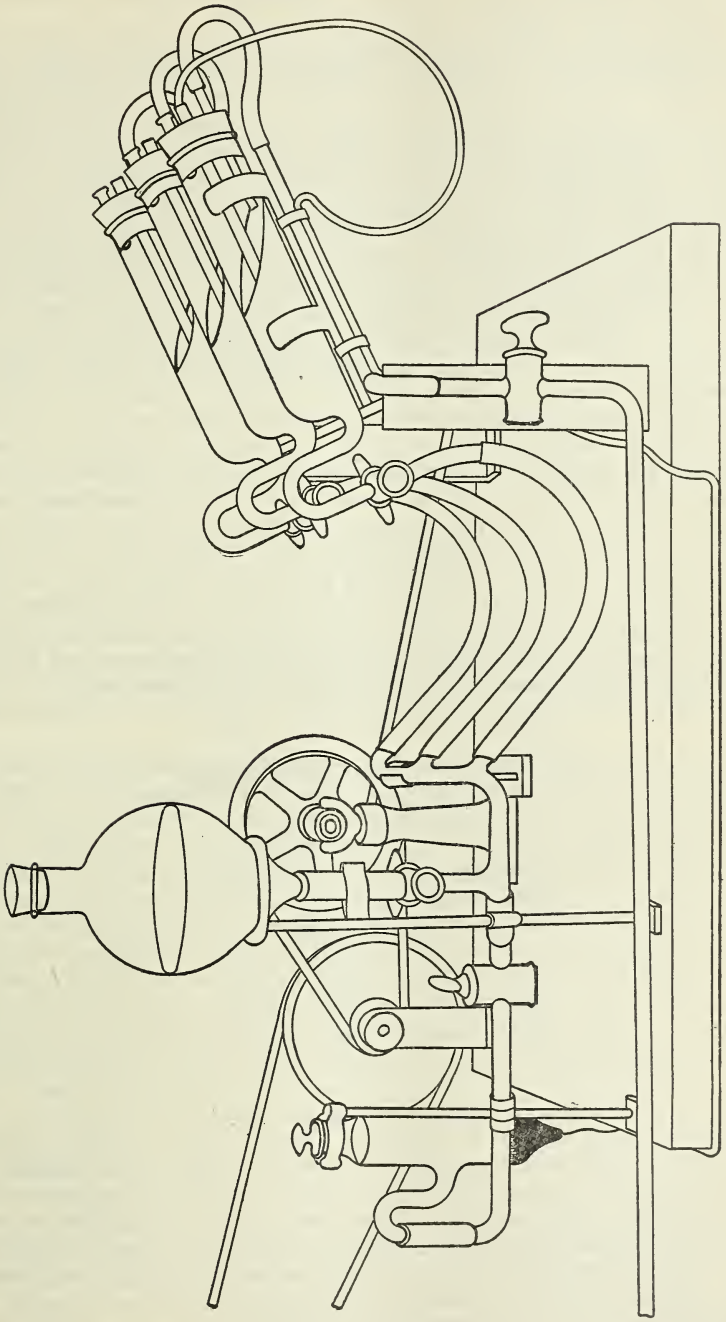

FIG. 3.—The electrometric system

A, figure 2. The end B is then carefully connected to the saturated calomel electrode by means of the connecting tubing, the entrance of air bubbles being avoided.

The remainder of the soil suspension is then poured into the vessel. The electrode (fig. 1) is lightly coated with palladium in about five seconds, is washed, electrolyzed in dilute sulphuric acid, and again thoroughly washed in distilled water. It is inserted into a rubber stopper containing an inlet and outlet for the hydrogen and then placed in the vessel. The space above the soil suspension is thoroughly swept out with pure hydrogen (*22*), which, however, is not bubbled through the suspension. While shaking, which is at the rate of about 80 complete swings a minute, contact with the calomel electrode is drawn into the end B and the potential is read (during shaking) (*60*) after 5-minute intervals, the second reading being in the nature of a control. Equilibrium is generally obtained in from 5 to 10 minutes (*60*). It has been observed that if the electrode vessel is not shaken during the measurement the potential sometimes increases so rapidly that any measurement would be a forced one, and readings made after the potential seemed to become constant would in general appear to be in error. The contact is drawn into the end B of the electrode vessel by opening the stopcock of the intermediate potassium-chloride reservoir (fig. 3), pinching the connecting tubing, closing the stopcock of the reservoir, and then opening the stopcock on the electrode vessel and releasing the pinch, thus preventing any possible entrance of potassium chloride into the soil suspension. All measurements were made with a high-grade potentiometer and galvanometer in connection with a Bureau of Standards certified Weston cell, temperature corrections being applied to all measurements which were made in a small room especially adapted to potentiometric work.

As a rule the reproducibility (*60*) of hydrogen-electrode measurements on soils has been within approximately 3 millivolts. It should be remembered, however, that the hydrogen electrode is not universally applicable, particularly in the presence of unsaturated substances and active oxidizing agents, and there may be soils containing constituents which would cause unsatisfactory results (*60*) and preclude the use of the hydrogen electrode. If such instances should present themselves in the case of soils, if there is reason to suspect the validity of the results, or if difficulty is had in obtaining stable and reproducible potentials with the hydrogen electrode, it is advisable to compare the hydrogen-electrode, quinhydrone-electrode, and colorimetric methods with one another. It has been the writer's experience during the past 10 years with thousands of soils that instances when the hydrogen electrode can not be used are few.

Regarding the effects of oxidizing agents such as nitrates, Joseph and Martin (*41*) observed that a neutral 1 per cent solution of sodium nitrate through which hydrogen was slowly passed for five hours in the presence of a few square centimeters of platinized platinum foil, reached a pH of more than 10 and gave a heavy precipitate with Nessler's reagent. These authors further state that no disturbing effect is likely to be introduced by nitrates up to 500 p. p. m. of soil. The effect of nitrates is further discussed by Sharp and Hoagland (*59*). These authors state that while with extracts of acid soils the

reduction of nitrates precludes the use of the hydrogen electrode it is not believed that appreciable errors would be caused in the case of nutrient solutions containing nitrates. Gillespie and Hurst (*33*) observed that the hydrogen-ion concentration of the extract comparatively free from soil particles was indefinite and meaningless, this being attributed to the presence of nitrates in a solution weak in buffer action.

A soil sample submitted to the writer gave with a hydrogen electrode a negative potential and a correspondingly absurd pH value for a soil. It was noticed that the box in which the soil had been sent was labeled "Bichloride of mercury." The treatment of 15 grams of a similar sandy soil low in organic matter with as little as 10 milligrams of $HgCl_2$ produced an effect greater than that mentioned above. This apparently was an instance of electrode poisoning. The effect on other soils higher in organic matter was comparatively small. A second sample of the original soil, but free from $HgCl_2$, was found to have a pH value of 5.3.

CALCULATION OF HYDROGEN-ELECTRODE RESULTS

The working formula for the computation of pH values, using the hydrogen electrode is:

$$\text{pH} = \frac{E - E_{(\text{cal.})}}{0.00019837\ T} \tag{1}$$

Where E = observed potential in volts.

$E_{(\text{cal.})}$ = potential between calomel electrode and normal hydrogen electrode at t centigrade. (Table 2.)

T = absolute temperature ($273.09 + t$ centigrade, observed).

TABLE 2.—*Calomel-electrode values*

[Referred to normal hydrogen electrode]

Temperature	KCl concentration		
	M/10	M/1	Saturated (approximate values)
°C.	*Volts*	*Volts*	*Volts*
18	0.3380	0.2864	0.2506
20	.3379	.2860	.2492
25	.3376	.2848	.2464
30	.3372	.2836	.2437
37.5	.3364		
40	.3360		

QUINHYDRONE-ELECTRODE METHOD

With the development of the quinhydrone electrode for practical use and its adaptation to soils by Biilmann (*7*) the use of this electrode has become rather extensive by virtue of the fact that coating of the electrode and the use of hydrogen are dispensed with and also because of its comparative simplicity and economy of time:

The essentials of this procedure are as follows: The soil treatment and filling of the electrode vessel are as described for the hydrogen-electrode method. After pouring the remainder of the soil suspen-

sion into the electrode vessel about 0.1 gram of quinhydrone (*5*, *60*) is added to the suspension, the plain platinum electrode (fig. 1), or preferably gold-foil electrode about 1 by 2 centimeters (*60*) is well washed with distilled water, inserted into a rubber stopper, and placed in the suspension in the electrode vessel. The vessel is shaken from one-half to one minute, after which the potential is immediately read with the vessel at rest, contact with the calomel electrode being made as described for the hydrogen electrode. The standard calomel electrode may be replaced by a standard quinhydrone electrode, as suggested by Veibel (*66*).

Various procedures and many types of quinhydrone electrodes have been developed for expediting this determination, the entire apparatus in many instances being available on the market. One procedure recommended by Biilmann and Jensen (*10*) is to prepare a large number of soil-water mixtures in test tubes. Add the quinhydrone to the first test tube, shake for two or three seconds, and place the test tube in a holder, inserting the electrode and the agar connecting tube. Now add quinhydrone to the next test tube, shake, then measure the potential of this first sample and remove. Now insert the second test tube in the holder, add quinhydrone to the third test tube, shake, and then read the second, and so on. These authors state that with some practice from 280 to 300 soil samples may be tested by one person in a 7-hour day. A standard equipment has been developed by Trénel (*63*) for agricultural work, employing a small porous cell as the standard, this cell containing a platinum electrode in a saturated solution of quinhydrone in 0.01N HCl and 0.09 N KCl. This cell is placed directly in the unknown solution and by a special arrangement the pH value may be read directly. Six hundred determinations were made in the course of 10 days without any appreciable alteration of the standard cell.

In a comparative study of the quinhydrone electrode with the hydrogen electrode made by the writer (*60*) many results on soils from about pH 4 to 9 show that the constancy of the quinhydrone electrode measurements may, with an occasional exception, be considered good. The quinhydrone electrode results showed in general good agreement with the hydrogen electrode, particularly on the acid side. On the alkaline side the larger variations were more frequent, although the quinhydrone electrode in some instances showed close agreement with the hydrogen electrode as high as pH 9.2. There were, however, some discrepancies between the quinhydrone and hydrogen electrode results on the acid as well as the alkaline side. Christensen and Jensen (*19*) determined the pH values of suspensions of many diverse Danish soils, ranging in pH values from approximately 3.5 to 8.5, and found close agreement between the hydrogen and quinhydrone electrodes. Baver (*5*) showed that the hyrogen and quinhydrone electrode results compare closely, the variation ranging from 0 to 0.2 pH. Working with soil suspensions Brioux and Pien (*16*), however, were unable to obtain in general the agreement between the two electrodes as reported by Christensen and Jensen. The agreement was better when using centrifugates, although the quinhydrone results were slightly higher, as a rule, and there still remained instances of unexplainable deviations. From the investigations of Olsen and Linderstrøm-Lang (*51*) it appears that

measurements made with the quinhydrone electrode on soil suspensions in some cases give a pH value of as much as 0.8 too high. The cases in question did not appear to be limited to any particular range of pH values, or to soils or localities of any particular character. In a communication from W. H. Pierre, of the Alabama Polytechnic Institute, it was stated that a number of soils with the quinhydrone electrode gave pH values 0.5 to 1.0 higher than did the hydrogen electrode or colorimetric methods. When the quinhydrone electrode was applied to soil extracts instead of soil suspensions good agreement with the other two methods was obtained.

LaMer and Parsons (*46*) working on buffer solutions found reliable results were obtained with the quinhydrone electrode in buffered solutions more acid than pH 8, provided no rapid oxidizing or reducing agents were present. Erroneous results obtained in more alkaline solutions are attributed to the autoxidation of hydroquinone. It is stated by Biilmann (*8*) (and this point should be kept in mind) that "the quinhydrone electrode is by no means a universal electrode, and there may be soils containing constituents which affect the electrode potential."

Owing to the lack of uniformity of conclusions obtained by these different investigators, further investigation of these at present unexplainable deviations with soils between the quinhydrone and hydrogen electrodes should be encouraged. This should not be construed as an indictment against the utility of the quinhydrone-electrode method, because the writer, although having observed discrepancies between results by the hydrogen and quinhydrone-electrode methods, due to the quinhydrone electrode, nevertheless has found good agreement in most instances and also excellent checks with the quinhydrone and colorimetric methods in a few cases (other than soils) where the hydrogen electrode was not applicable. And further, as shown by Biilmann (*7*), when the percentage of nitrates is sufficiently high to interfere with the obtainment of constant potentials due to reduction by the hydrogen electrode, this factor will not preclude the use of the quinhydrone electrode. It is quite apparent, therefore, that in precise work if the investigator has the least suspicion of the validity of his results he should, as previously stated, compare the hydrogen-electrode, quinhydrone-electrode, and colorimetric methods with one another.

CALCULATION OF QUINHYDRONE-ELECTRODE RESULTS

The potential-temperature curve of the quinhydrone electrode over the range 0°, 18°, 25°, and 37°, respectively, was found by Biilmann and coworkers (*8*, *11*, *12*) to be practically a straight line represented by the following equation:

$$\pi_t = 0.7175 - 0.00074\ t \tag{2}$$

By a simple substitution in which E in equation (1) is replaced by $\pi_t - E_q$ where E_q is the observed potential difference between the quinhydrone and calomel electrodes, the working equation for the quinhydrone electrode becomes,

$$\mathrm{pH} = \frac{\pi_t - E_{(\mathrm{cal.})} - E_q}{0.00019837\,T} \tag{3}$$

When using either the saturated, normal, or tenth-normal calomel electrodes there is a current reversal at a definite pH value depending on the electrode used and on the temperature. From equation (3) it is obvious that with the tenth-normal calomel electrode at 18° C. the potential is zero at approximately pH 6.34 and negative with increasing pH. Using the saturated calomel electrode at 18° this change of potential from positive to negative occurs at about pH 7.86. With soils below pH 7.86 the observed potentials, when using the saturated calomel electrode, will be positive, since the quinhydrone electrode will be positive to the calomel electrode. With soils above pH 7.86 the potentials will be negative.

The sign of the observed potential difference is that of the quinhydrone electrode in relation to the known sign of the standard calomel electrode. Referring the observed potentials to the sign of the calomel electrode, then $-E_q$ in equation (3) becomes $+E_q$.

THE ANTIMONY ELECTRODE

The antimony electrode was employed by Uhl and Kestranek (*65*) for analytical neutralizations and later an extensive study of its properties was made by Kolthoff and Hartong (*44*). Later Franke and Willaman (*27*) made a study of the antimony electrode and applied it to the determination of the hydrogen-ion exponents of paper-mill liquors. As the use of this electrode dispenses with the necessity of plating electrodes and the use of hydrogen and quinhydrone, it tends to simplify and expedite the determination as compared to the customary electrometric procedures.

PREPARATION OF ANTIMONY ELECTRODE

Kolthoff and Hartong (*44*) used for their electrode antimony analyzing 99.97 per cent antimony. This was melted and poured into a rodlike mold. These investigators obtained more reliable results and constant potentials more rapidly when a little antimony trioxide was added. According to Uhl and Kestranek (*65*), whose results Kolthoff and Hartong also confirmed, the antimony contains sufficient antimony oxide so that any further addition is unnecessary.

For the determination of the hydrogen-ion exponents of soils (*61*), the writer has used stick antimony purchased as C. P. and measuring about 7 millimeters in diameter and cut into 4-centimeter lengths. Many electrodes were used as such and were also recast from this antimony, while a number of electrodes were also cast from a sample of antimony obtained from the United States Bureau of Standards. This antimony analyzed Sb, 99.94 per cent; Pb, 0.05 per cent; Fe, 0.013 per cent; Cu, none; Sn, none; Zn, none; and As, a trace. Other electrodes were made by melting this antimony in a crucible and pouring it into a pyrex tube sealed at one end. With others the tube was embedded in a heated sand bath. There is sufficient evidence to indicate that the purity as well as the crystallization and heat treatment of the antimony are factors contributory in part at least to the constancy and reproducibility of the potentials. In most instances these electrodes were about 5 centimeters long and 7 millimeters in diameter. They were filed fairly smooth and then polished on a buffing wheel. The electrodes took on a very bright

finish, but gradually oxidized with use. In this respect Franke and Willaman (*27*) state that a bright electrode no doubt gives a quicker response than a tarnished one, but shows more tendency for a potential drift; consequently they recommend a tarnished electrode for all purposes. Connection was made to the electrodes by soldering to a copper wire and the electrodes were then securely held in place in a pyrex tube with sealing wax after a shoulder had been ground on the electrode.

ANTIMONY-ELECTRODE METHOD

With the antimony electrode the procedure used by the writer is as follows: The soil treatment and filling of the electrode vessel are as described for the hydrogen and quinhydrone-electrode procedures. The plain antimony electrode is well washed with distilled water, inserted in a rubber stopper, and placed in the vessel. The vessel is shaken about one or two minutes, and the potential is read during agitation, as in most instances the potential read after bringing the vessel to rest drifted rapidly.

It is stated by Kolthoff and Hartong (*44*) that in order to obtain reliable results the liquid must be stirred during the determination. The stirring was accomplished by a stirrer or by the passage through the solution of an indifferent gas such as nitrogen or hydrogen. Uhl and Kestranek (*65*) state that the chief reason for the deviation from the correct titration results was due to the influence of the carbon dioxide of the air, and accordingly they used carbon-dioxide-free air for agitation. It was concluded by Franke and Willaman (*27*) that both oxygen and carbon dioxide can affect the potential, but that the magnitude of the effect is small unless these gases are actually bubbled through the solution. The vessel used by the writer (fig. 2) is a closed type of shaking electrode vessel and consequently avoids any undue contact of the soil suspension with the atmosphere.

The reproducibility and constancy of potentials may be considered very good for soils. Equilibrium is generally obtained in about one minute. Constant potentials were generally obtained by Uhl and Kestranek (*65*) in about 30 seconds while Kolthoff and Hartong (*44*) and Franke and Willaman (*27*) obtained constant potentials within about two minutes.

Some preliminary results from about pH 3.6 to 9.2 between the hydrogen and antimony electrodes showed very good agreement for the soils investigated. Further work will be necessary to determine the applicability of the antimony electrode to the determination of the hydrogen-ion exponents of soils in general.

CALCULATION OF ANTIMONY-ELECTRODE RESULTS

The equations given by Kolthoff and Hartong (*44*) for measurements against the N/1 calomel electrode at 14° C. are as follows:

(4) $E=0.0415+0.0485$ pH, (from pH 1 to 5)
(5) $E=0.009+0.0536$ pH, (pH above 9)

The equation given by Franke and Willaman (*27*) for potentials measured against the N/1 calomel electrode is as follows:

(6) $E=0.050+0.054$ pH, at 25° C.

The saturated calomel electrode was used by the writer and all measurements were made in a room kept at approximately 25° C. during the course of the determinations, the results being calculated from equation (6) after correcting the saturated calomel electrode potentials to the N/1 calomel electrode.

OUTLINE OF COLORIMETRIC METHODS

The colorimetric procedure for the approximate determination of the hydrogen-ion concentration depends on the fact that an indicator exhibits a gradual color change over a characteristic range of hydrogen-ion concentration. On the acid side of this range, the indicator exhibits its acid color and then passes through its mid or neutral point to the alkaline side where it is transformed into its alkaline color.

In the colorimetric determination of hydrogen-ion concentrations the standard solutions used are termed "buffer solutions." Buffer action may be defined as the resistance offered by a solution to a variation in its pH value as a result of the addition or loss of acid or alkali. These buffer solutions are generally mixtures of some acid and its alkali salt. The pH values of the solutions are accurately determined by the hydrogen electrode. A detailed discussion of indicators and buffer solutions has been given by Clark (*22*) so its repetition is unnecessary. As many colorimetric methods are to be found in the literature, reference will be made to only a few which embody different principles.

Clark (*22*) makes use of a series of accurately prepared and electrometrically standardized buffer solutions which, with the added indicator, are compared with the solution under investigation containing the same indicator concentration.

The double-wedge principle of Bjerrum (*14*) has of late been used as a colorimetric method and consists of two wedges, one containing the indicator in the acid form and the other containing it in the alkaline form. A view through these wedges should give the intermediate colors of the indicator. An attached scale gives the pH values for the corresponding colors with which the unknown is compared.

A set developed by Morgan (*49*) for use in the field or laboratory consists of a small porcelain block with a depression near the top of its sloping surface, divided into two parts separated by means of a perforated wall. From the lower part of this depression a channel runs to near the bottom of the sloping surface, where it ends in another depression. The lower part of the upper depression is filled with soil, and a few drops of indicator solution are added. After passing through the soil and into the depression at the bottom, the solution is compared with a printed color chart. Out of 626 soils tested by this method, Morgan found that 86 per cent of the soils agreed within 0.3 pH or less with the quinhydrone electrode determination. Some difficulty, however, has been experienced in matching the color of the unknown, due in part at least to its turbidity and to the fading of the printed color standards.

Gadd (*28*) has described a method for the determination of the pH values of turbid soil and other solutions, the basic principle of which

was previously used by Atkins (*2*). Two parts of water and one of air-dried soil are shaken in a vessel for 10 minutes and are allowed to stand for 24 hours. About 3 cubic centimeters of the indicator solutions recommended by Clark (*22*) are required for 25 cubic centimeters of the soil solution. If the solution is very turbid the amount of indicator may be doubled. Equal quantities (about 5 cubic centimeters) of the colored samples are placed in suitable tubes of uniform bore and 10 drops of distilled water are added to one of the tubes, used as a control. Ten drops of a known buffer solution are added to another tube, and the resulting color is compared with that of the control. If no alteration in color occurs, the soil solution and buffer have the same pH; if there is a color change, other buffer solutions are tried. If one buffer is too acid and the other too alkaline, then the pH may be estimated by interpolation. If the turbidity of the soil solution is such as to make it difficult to determine which buffer has caused the least alteration in color, the control and buffered tubes in question may be diluted with equal quantities of distilled water and again compared.

Gillespie (*31*) described a colorimeter for the determination of hydrogen-ion concentrations, consisting of three concentric vessels on one side and two on the other. Of the three vessels the middle movable one contains the acid form and the lower one the alkaline form of the indicator. The position of the center vessel obviously determines the ratio of the acid and alkaline forms of the indicator. The top tube may be used for turbidity compensation. Of the two vessels on the other side the lower one contains the unknown with indicator. The writer has applied Gillespie's principle to the Duboscq colorimeter for the determination of pH values and has obtained excellent results. There has recently appeared a combination standard and pH colorimeter similar in principle to Gillespie's and having an electric lamp and daylight filter in the base of the instrument with an illuminated table for the calculation of results.

A recently introduced comparator consists essentially of a wooden drum holding the buffer solutions and revolving inside of a metal band. A block holding three test tubes is fastened to the front of the band, and by the aid of an electric lamp and a dalight glass comparisons are made by revolving the drum.

Another form of comparator consists of a color disk with standard color plates of glass for different indicators, the disks being arranged in a revolving circle.

The drop-ratio method of Gillespie (*30*) avoids the preparation of and electrometric standardization of buffer solutions. As this method has been rather widely used and requires little preparation other than the indicator solutions it will be described later in detail.

When using the colorimetric procedure, turbidity and color of the extract are interfering factors which, together with the human element, eye differences, and eye fatigue, lend both difficulty and uncertainty to the colorimetric method. For practical purposes the colorimetric procedure may be sufficiently accurate, but for a more precise determination the fundamental hydrogen-electrode method should be used when applicable.

OBTAINING THE SOIL EXTRACT

For obtaining the soil extract for colorimetric determinations, such methods as centrifuging, filter paper, Pasteur-Chamberland filters, flocculating agents, suction filters, and dialysis through collodion sacks have been used.

Using an electric centrifuge for clarifying soil extracts Gillespie and Hurst (*33*) found that the electrometric and colorimetric results on a large number of soils agreed within the experimental error. Atkins (*3*), using a centrifuge capable of running at 9,000 revolutions per minute, but usually run at a slower speed, obtained clear solutions for almost all soils, although a few remained slightly turbid. The use of the centrifuge, where possible, is recommended by Atkins. Results obtained by Pierre (*52*) show an increase of 0.25 pH, due to centrifuging a clear soil extract in an open test tube, but no change when it is centrifuged in a closed test tube. Working with filtered soil extracts, Gillespie and Hurst (*33*) observed that soil extracts filtered through filter paper were incorrect and variable, according to the brand and treatment of the paper. Barnette, Hissink, and Van der Spek (*4*) found that filtrates (obtained through paper and "bougies") of suspensions of the four soils studied were acid, but always less acid than their corresponding suspensions.

Atkins (*3*) concluded that the pH values of some soil extracts are markedly modified by filtration, even when a first filtrate is rejected. The acidity may be reduced by both untreated and acid-extracted filter papers. It was observed by Atkins that the rejection of a large first filtrate, about 160 cubic centimeters, lessened the error resulting from filtration.

Nehring (*50*) compared the pH determinations of soils made on suspensions (quinhydrone electrode) and filtrates and found widely deviating results by the use of different filter papers. Accordingly, Nehring states that the use of filtrates should be avoided. However, if filter paper must be used, only quantitative filter paper which has been repeatedly washed with boiled distilled water should be employed. Results obtained by the writer with Pasteur-Chamberland filters showed an increase in acidity with four alkaline soils as a result of filtering. These results are in agreement with those obtained by Fisher (*26*), who observed that soil extracts filtered through paper or Pasteur-Chamberland thimbles became more acid as filtration proceeded. Fisher shook 50 grams of soil and 100 cubic centimeters of conductivity water one hour and centrifuged the supernatant liquid at 3,000 revolutions per minute. Pierre and Parker (*54*) used a Pasteur-Chamberland filter and found a change in pH from 4.7 to 5.7 on one soil and no change on another. Gillespie (*30*), using colloidal iron for the clarification of soil extracts, found that the extracts so obtained (from nine acid soils) gave the same results as were obtained by the usual methods, but he did not feel justified in recommending this procedure on the basis that other soils with probably less buffer action might possibly be changed by the residual acidity of the colloidal iron used. Kühn (*45*) used a special grade of barium sulphate as a clarifying agent, but the limit of exactness was 0.5 pH. Using a modified suction apparatus as devised by Truog (*64*), Pierre and Parker (*54*) found that the colorimetric results on these filtered soil extracts, collodion sack extracts, and the

electrometric results on soil suspensions agree well. The filter paper was washed 10 or 15 times with hot conductivity water, was dried at 50° C., and stored in a desiccator. Regarding the use of collodion sacks, Pierre and Parker (*54*) conclude that this method of obtaining soil extracts is short, simple, and gives the soil extract in an unaltered condition.

DETAILS OF THE DROP-RATIO METHOD

Briefly stated, the drop-ratio method consists in the comparison of the soil extract containing a definite quantity of indicator with pairs of standards, each pair containing 10 drops of the same indicator, which is distributed in the tubes in the ratio of 1 drop in one and 9 in the other, 2 to 8, 3 to 7, and so on to 9 to 1. The indicator in the front row of tubes is transformed to its alkaline color, and in the other row it is transformed to its acid color. The experimental standardization of the method and the theoretical equation for an indicator acting as a monobasic acid, relating the hydrogen-ion exponent and drop ratio, have been previously described by Gillespie (*30*).

PREPARATION OF INDICATOR SOLUTIONS

In Table 3 are given the percentage strengths of the various indicator solutions in terms of the free-acid indicator, together with the quantities of alkali necessary to form the monosodium salts. The weighed amount of the indicator is ground in an agate mortar (avoid a glass mortar) (*52*) with the standard alkali. At first the indicator is just moistened, then is made up to volume with distilled water and stored in pyrex bottles. The standard alkali is given in 1.1 equivalents for all indicators except bromcresol purple, in which case 1.5 equivalents are used. Bromcresol green (*23*, *39*) has been substituted in place of methyl red used by Gillespie (*30*). This indicator, being more stable than methyl red, which is easily reduced, completes a series of sulfonphthalein indicators.

TABLE 3.—*Data for the determination of the hydrogen-ion exponent by the drop-ratio method*

Drop ratio	Hydrogen-ion exponent for each pair of tubes						
	Bromphenol blue	Bromcresol green	Bromcresol purple	Bromthymol blue	Phenol red	Cresol red	Thymol blue
1 to 9	3.1	3.7	5.3	6.15	6.75	7.15	7.85
1.5 to 8.5	3.3	3.9	5.5	6.35	6.95	7.35	8.05
2 to 8	3.5	4.1	5.7	6.5	7.1	7.5	8.2
3 to 7	3.7	4.3	5.9	6.7	7.3	7.7	8.4
4 to 6	3.9	4.5	6.1	6.9	7.5	7.9	8.6
5 to 5	4.1	4.7	6.3	7.1	7.7	8.1	8.8
6 to 4	4.3	4.9	6.5	7.3	7.9	8.3	9.0
7 to 3	4.5	5.1	6.7	7.5	8.1	8.5	9.2
8 to 2	4.7	5.3	6.9	7.7	8.3	8.7	9.4
8.5 to 1.5	4.8	5.4	7.0	7.85	8.45	8.85	9.55
9 to 1	5.0	5.6	7.2	8.05	8.65	9.05	9.75
Per cent in indicator solution	0.008	0.015	0.012	0.008	0.004	0.008	0.008
C. c. 0.1 N NaOH per 0.1 gram portion	1.64	1.58	2.78	1.77	3.10	2.88	2.38
Produce acid color with	0.05N HCl	0.05N HCl	0.05N HCl	0.05N HCl	0.05N HCl	2 per cent KH_2PO_4	2 per cent KH_2PO_4
	1 c. c.	1 drop	1 drop	1 drop	1 drop	1 drop	1 drop
Produce alkaline color with 0.05 N NaOH	1 drop	1 drop	1 drop	1 drop	1 drop	1 drop	2 drops

Atkins (*3*) states that the indicators should be used in their half-transformed condition, this being of particular importance when dealing with lightly buffered soil extracts or natural waters. Pierre (*52*) states that in working with slightly buffered solutions as the soil solution the indicators must be absolutely neutral. In an earlier article by Birge and Acree (*13, p. 1037, note 1*) it is stated that by titrating the solutions of the monobasic salts of the sulfonphthalein indicators with more alkali and so adjusting the indicator solutions to any desired pH value it is possible to mix the indicator with a solution known to have approximately the same pH value and thereby obviate any appreciable change of the pH, even when the solution has weak buffer properties.

In a recent article by Pierre and Fudge (*53*) it is stated that in order to obtain accurate results when working with slightly buffered soil extracts or unbuffered solutions of any kind, the pH values of the indicator solutions should be adjusted so as to correspond to a pH value near the middle of the transition interval of the indicator. The pH values used by Pierre and Fudge are bromphenol blue, 3.80; bromcresol green, 4.60; bromcresol purple, 5.80; bromthymol blue, 6.80; and phenol red, 7.60. For determining the pH values of the indicator solutions these authors used with satisfaction the quinhydrone electrode in preference to the hydrogen electrode with which they had difficulty in obtaining constant potentials. Pierre and Fudge also used the varying drop method, in which 3, 5, and 8 drops of indicator are successively added to a weakly buffered solution and also to a standard buffer solution. If the pH value of the weekly buffered solution changes toward the acid side, as compared with the standard buffer solution, it shows that the indicator solution is more acid than the unbuffered solution.

By the addition of acid or alkali to the indicator solutions until slightly buffered solutions show no change, whether 3 or 8 drops of the indicator solution are added, adjustment of the indicator solutions can be made to the desired pH value. This method is obviously more tedious than the electrometric method. The procedure of either having the indicator solution and unknown solution isohydric or of bringing the indicators to their half transformation points is an important factor when dealing with very weakly buffered solutions. However, most soil extracts are sufficiently buffered so as not to be affected by the indicator solutions made up as described by Clark (*22*). For very precise work the isohydric principle may be desirable.

The isohydric indicator method (*13, p. 1037, note 1*) is the use of an indicator solution made up to the same pH as the unknown in order to prevent the unknown and the indicator from changing each other and to give a final color-buffer mixture (unknown or standard plus indicator) at the same pH as the unknown (or standard if used). The procedure devised by Miss Fawcett, of the United States Department of Agriculture, and S. F. Acree, of the United States Bureau of Standards, for the preparation and use of isohydric indicators is as follows: Indicator solutions are made up as M/1,000 or 0.02 per cent or any desired concentration of the monobasic salt, or brought to the first faint color change with N/10 NaOH or HCl; 50 or 100 cubic centimeter portions are put into individual pyrex

flasks and adjusted as follows: As an example, take bromthymol blue covering the pH range 6 to 7.6. Add to a clean pyrex test tube 0.2 of a cubic centimeter or less (even 0.05 of a cubic centimeter) of a pH 6 buffer solution and 0.2 of a cubic centimeter of the indicator solution and stopper the test tube, which is then laid on its side as the buffer-color standard. Then 0.2 of a cubic centimeter of the indicator is put into another clean pyrex test tube of the same bore and stoppered and laid beside the other test tube whereby the colors are compared. If the pH of the indicator solution is below or above the pH 6 buffer-color standard, it is adjusted by cautiously adding small volumes of N/10 NaOH or HCl until the color of 0.2 of a cubic centimeter just matches the buffer-color standard. The next stock of pH 6.2 indicator is similarly prepared by comparison with a pH 6.2 buffer-color standard. In this way the ranges of the different indicators may be covered in steps of 0.2 pH. Of course, some samples of the indicators are impure and these solutions do not always keep indefinitely, but restandardization can easily and quickly be made. As a rule, the change in pH of these stock solutions between use and occasional restandardization is small.

The isohydric indicators are used as follows: Add to 10 cubic centimeters or other desired volume of the unknown 0.2 of a cubic centimeter or other necessary volume of the various indicators adjusted to their midpoints and determine the approximate pH by comparison against the usual buffer-color standards or the drop-ratio standards. The buffer-color standards are prepared by adding to 10 cubic centimeters of the buffers 0.2 of a cubic centimeter of the corresponding isohydric indicator. If the approximate pH of the unknown is below the indicator midpoint, then to a second sample of the unknown add the next isohydric indicator lower than the approximately determined pH. If the approximate pH is above the indicator midpoint, add the next isohydric indicator higher than the approximately determined pH. If the unknown is well buffered, these two tests will give practically the same pH. If the unknown is weakly buffered the two tests may vary 0.1 to 0.2 pH, depending on the buffer capacity of the unknown and the divergence of its pH from that of the midpoint indicator, and a third test may be necessary. If the pH of the second test was farther from the indicator midpoint than the isohydric indicator used in the second test, then the indicator for the third test is the next one farthest from the midpoint. If the pH of the second test was nearer the indicator midpoint than the isohydric indicator used in the second test, then the indicator for the third test is the next one nearest the indicator midpoint. This quickly gives two "unknown-color mixtures" whose pH values are between those of the two indicators used therein, and it is easy, by comparison with the color standards, to judge the correct pH of the unknown. Data have also been obtained which take into account the salt errors involved in the use of the buffer standards.

PREPARATION OF COLOR STANDARDS FOR THE DROP-RATIO METHOD

The test tubes used for the color standards are approximately 1.5 centimeters external diameter and 15 centimeters long, preferably without flanges. Sufficient uniform test tubes should be selected by

pouring 10 cubic centimeters of water into each and retaining those which are filled to the same heights or within a few millimeters. The test tubes may be weathered by boiling for one-half hour in chromic-acid solution. Test-tube racks having two rows are used for holding the pairs of standards. To prepare a set of standards for any indicator 1 drop of the indicator is placed in the first test tube and 9 in the rear one, 2 in the second and 8 in the rear one and so on up to 9 in the last and 1 in the rear. In Table 3 are given the quantities of alkali to be added to the front row of test tubes to develop the alkaline color and the quantities and type of acid to be added to the rear row to develop the acid color, the strengths being only approximate. The volume is now made up to a height corresponding to 5 cubic centimeters. The 1.5 to 8.5 ratio, when needed, is prepared by using 3 and 17 drops, respectively. Before preparing a color standard it is advisable to test 1 cubic centimeter of the unknown with 2 drops of the different indicators. After having become familiar with the color changes and useful ranges of the different indicators it is a comparatively simple matter to ascertain which indicator to employ in the preparation of the standards.

DROP-RATIO METHOD

Having determined the indicator to be used and having prepared the color standards, 10 drops of the indicator are added to a test tube and sufficient of the centrifuged soil extract is added to bring the volume up to a height corresponding to 5 cubic centimeters. The centrifugate is obtained by centrifuging for about 15 minutes at approximately 3,000 revolutions per minute, the supernatant liquid from 15 grams of soil and 30 cubic centimeters of water which has been shaken vigorously about one minute in a large pyrex test tube and allowed to stand about 20 minutes or longer for sedimentation.

The test tube containing the centrifugate and indicator is placed in the comparator (fig. 4) and compared with different pairs of the color standards until its position relative to the color standards is located.

The comparator clearly shown in Figure 4 is an adaptation of the principle of Walpole (*67*) and in brief consists of a block of wood with two rows of holes of three each, through each row passing a smaller view hole. The test tube holes, which should lie in the indicated planes and should be as close as possible, will accommodate test tubes a trifle smaller in external diameter than five-eighths of an inch. The interior is painted flat black. Considering the top view of the comparator (fig. 4) two test tubes of water are placed in the two upper left-hand holes and the unknown with indicator in the lower left-hand hole. The test tube containing the unknown solution without indicator, to compensate for turbidity, is placed in the upper right-hand hole and the pair of color standards in the lower right-hand holes. The view may be made against the clear sky. It is essential to work within the ratios 1:9 and 9:1, since the percentage transformation of the indicators at these points is such that the hydrogen-ion exponent of the unknown may be different from that indicated by the ratio, without a color difference being present to show this. It may so happen that the color of the unknown does

not match exactly a pair of standards, in which instance its intermediate position between two pairs of standards is located, and from Table 3 the value of the hydrogen-ion exponent is read. If when working with bromcresol purple the dichromatism of the indicator becomes such a disturbing factor that it is difficult to obtain a match, the tubes may be viewed against a yellow light as suggested by Clark (*22*). Use is made of a box containing a carbon-filament electric light, the rays passing through tracing paper stained yellow by painting with a solution of 5 cubic centimeters of a 0.6 per cent solution of phenol red and 5 cubic centimeters of M/5 KH_2PO_4. To

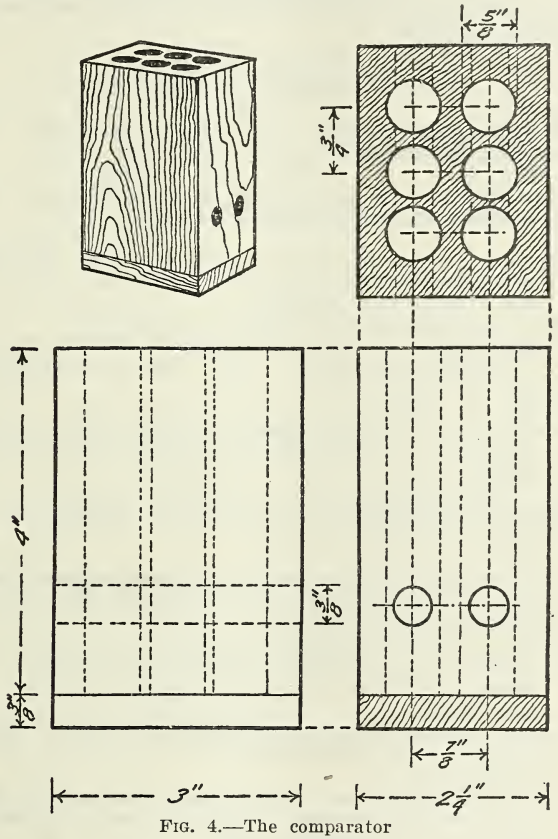

FIG. 4.—The comparator

avoid the dichromatism of bromcresol purple, bromphenol red or chlorphenol red (*23*) may be used advantageously, as their ranges are similar to that of bromcresol purple.

In a paper by Hatfield (*35*) a modification of Gillespie's method is offered in which buffer solutions are used for producing the acid and alkaline colors of the indicators. It is claimed that the color standards are more permanent under these conditions. In regard to the permanency of the color standards, Gillespie (*30*) states that it would appear that no change whatever need be feared during the first day, except possibly in the case of cresol red and thymol blue, this apparently being dependent on the laboratory atmosphere.

SUMMARY

Electrometric and colorimetric methods for the determination of the hydrogen-ion concentration of soils, including the hydrogen, quinhydrone, and antimony electrodes, and numerous colorimetric methods, particularly Gillespie's drop-ratio method, are described in detail.

The factors affecting the hydrogen-ion concentration of soils, such as the periodic variation of hydrogen-ion concentration, drying, grinding, the soil-water ratio, carbon dioxide, and the methods of obtaining the soil extract are discussed, along with such other incidental data as will be helpful in the determination of the hydrogen-ion concentration of soils.

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